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A rapid procedure for the determination of thorium, uranium, cadmium and molybdenum in small sediment samples by inductively coupled plasma-mass spectrometry: application in Chesapeake Bay

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Abstract

This paper describes a rapid procedure that allows precise analysis of Mo, Cd, U and Th in sediment samples as small as 10 mg by using a novel approach that utilizes a “pseudo” isotope dilution for Th and conventional isotope dilution for Mo, Cd and U by ICP-MS. Long-term reproducibility of the method is between 2.5 and 5% with an advantage of rapid analysis on a single digestion of sediment sample and the potential of adding other elements of interest if so desired. Application of this method to two piston cores collected near the mouth of the Patuxent River in Chesapeake Bay showed that the accumulation of authigenic Mo and Cd varied in response to the changing bottom water redox conditions, with anoxia showing consistent oscillations throughout both pre-industrial and industrial times. Accumulation of authigenic U shows consistent oscillations as well, without any apparent increase in productivity related to anoxic trends. Degrees of Mo and Cd enrichment also inversely correlate to halophilic microfaunal assemblages already established as paleoclimate proxies within the bay indicating that bottom water anoxia is driven in part by the amount of freshwater discharge that the area receives.

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1. Introduction

To what extent sedimentary concentrations of redox sensitive elements can be used to infer past conditions of depositional environments has long been of interest to marine geochemists (Calvert and Pedersen, 1993). To generate high-resolution redox element records for paleoceanographic application, it is desirable to apply a methodology that can analyze geochemical suites of redox sensitive elements in small samples (e.g., 10 mg)

both rapidly and simultaneously. Although Th is not a redox sensitive element, simultaneous determination of Th concentration is needed because it allows for the estimation of the authigenic component of the redox sensitive metals.

In previous work, U and Th in marine sediments have been analyzed mostly by alpha spectrometry (Anderson and Fleer, 1982), and Cd and Mo by graphite furnace atomic absorption spectrophotometry (GFAAS) (Boyle and Edmond, 1975; Parker, 1983; Segar and Cantillo, 1975). Each element required a different sample pre-treatment and separation procedure that is often time consuming. In addition, because they are not analyzed simultaneously, the total sample size required is larger.

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This is true particularly for U and Th analyses, where 500 mg samples are often needed to obtain a 5% precision. The development of the inductively coupled plasma mass spectrometer (ICP-MS) has made possible the rapid, precise and simultaneous measurements of many trace elements. For example, analysis for 11 elements including Mo, Cd, and U by isotope dilution ICP-MS was successfully performed on marine sediment standard reference materials, however, a large sample size of 500 mg was used (McLauren et al., 1987). Here, the authors show that the isotopic dilution ICP-MS analytical method can be applied for rapid trace metal (Mo, Cd, and U) analyses using marine sediment samples as small as 10 mg. Furthermore, it is demonstrated that Th can be quantified using a U-isotope spike (pseudo-isotope dilution) and does not require a Th isotope spike. The method is easy to use, rapid, and allows for the addition of many other elements of interest. The main advantage of isotope dilution and small sample size for each redox element analyzed is that the matrix effect and other secondary effects are minimized, and therefore the quality of data over long periods of time is improved. Analysis of marine sediment samples from Chesapeake Bay demonstrates the potential for using Mo and Cd for paleo-oxygenation reconstruction and U for paleo-productivity reconstruction.

2. Experimental methods

2.1. Sample spiking and digestion

Enriched isotopic spikes of ^{95}Mo in metal form, ^{111}CdO and $^{236}\text{UO}_2$ are from Oak-Ridge National Laboratory (ORNL). About 10 mg of ^{111}CdO was dissolved in 5 ml of concentrated HNO_3 (Seastar) overnight, and diluted with 95 ml of nanopure water (~ 18 Mega Ω). ^{95}Mo and ^{236}U spikes were prepared following the same procedure except that both required heating to about 100 °C. The working secondary spike solution containing ~ 700 ng Mo/g, ~ 200 ng Cd/g and ~ 130 ng U/g were calibrated against standard solutions prepared by diluting SPEX ICP-MS standard Mo, SPEX AA standard Cd and a Lamont-Doherty TIMS lab calibrated ^{233}U solution respectively. Cross contamination was checked for all the isotopes in the measurement procedure and was found to be at the ICP-MS background level.

One hundred microliters of a secondary spike solution were first pipetted into a 50 ml Teflon beaker and the weight of the spike was recorded. About 10 mg of freeze dried and ground marine sediment sample were accurately weighed into the beaker. The procedure for a rapid digestion of small samples (~ 10 mg) is a modification of an earlier method (Fleisher and Anderson, 1991).

The sample was brought into solution as follows: (1) 0.75 ml of ultra pure concentrated HClO_4 (Fisher Optima) was added to the Teflon beaker to be heated on a hot plate until the dense, white HClO_4 fume is visible. Fuming was allowed to continue for about 10 min. (2) 1.0 ml of ultra pure concentrated HF (Fisher Optima) and 1.0 ml of concentrated HNO_3 (Fisher Optima) were added. The heating and fuming was resumed until the sample volume was reduced to about a 50 μl . At this point, the drop should be clear and overheating was avoided. (3) 20 ml of 1% HNO_3 (Fisher Optima) was added to dissolve the digested sample. (4) The digested sample was transferred into a 14-ml Polypropylene round-bottom tube (Falcon) with polyethylene cap. The analysis was performed within 24 h of sample digestion when possible.

Two or 3 procedure blanks were usually prepared together with a batch of 35 samples. A sediment sample collected in Santa Barbara Basin (MCE-PB6) was included in every batch of digestions for quality control. The procedure must be performed in a HClO_4 and HF hood, using care to avoid acid burns. The acid digestion procedure can be completed within 3 h.

2.2. Description of elemental determination

Measurements were made on a VG Elemental Plasma Quad 2+ Turbo ICP-MS at Lamont-Doherty. The instrument achieves an average count rate of 30,000 cps (counts per second) for a 1 ppb In solution (0.1% HNO_3) under standard instrument operating conditions. The VG plasma Quad 2+ is operated according to the standard recommended conditions. The acquisition mode is pulse counting with a dwell time of 10.24 ms and a 3 points peak jumping. The acquisition time is 60 s, with at least 90–120 s of wash time between samples. Sufficient count rates can be achieved using a standard V-Groove nebulizer at a flow rate of about 0.8 ml/min. A typical analysis includes spiked procedural blanks and samples, interspersed with 0.1% HNO_3 and 1% HNO_3 blanks. A mixed standard of Cd and Mo, and a solution containing a NBS U-500 standard, which has an $^{235}\text{U}/^{238}\text{U}$ ratio of 0.9997, are run before and after the sample analysis procedure to monitor the mass bias effect.

2.2.1. Uranium and thorium

A synthetic isotope ^{236}U is used as the spike and ^{238}U is used as the quantification isotope. No isobaric interference is known or has been observed. The Th concentration is also calculated using ^{236}U as the spike and ^{232}Th as the quantification isotope, following an approach that can be regarded as internal standardization or pseudo-isotope dilution. Since Th has a strong tendency to sorb to solid surfaces, analysis should be completed within 24 h of sample digestion; however,

repeated analyses of the same batch of samples after 1 week of storage showed no difference of Th concentrations from those which were analyzed immediately after digestion. Comparison of Th results obtained by ^{230}Th ID and ^{236}U pseudo-ID ICP-MS indicate that reasonable Th measurements can be achieved using ^{236}U as an internal standard (Fig. 1). The reasons for choosing ^{236}U over ^{230}Th as spike for Th analyses will be discussed later (see Section 3.2.2).

2.2.2. Molybdenum and cadmium

For Mo, isotope ^{95}Mo is used as the spike and ^{98}Mo is chosen as the quantification isotope. Cadmium is the only element among those included in this study which may suffer from insufficient sensitivity when the Cd concentration in the marine sediment is approaching the crustal average value of $0.1\ \mu\text{g/g}$. Fortunately, the concentration of Cd in the marine sediments analyzed is usually greater than $0.3\ \mu\text{g/g}$. The spike isotope is chosen to be ^{111}Cd . ^{113}Cd is preferred over ^{114}Cd for quantification of marine sediment analysis due to lower isobaric interference from ^{114}Sn . The effect of isobaric interference on Mo and Cd analysis is discussed later (Section 3.1.3).

3. Results and discussions

Isotope dilution (ID) analysis is generally accepted as the most precise form of standardization. However,

accurate calibration of the isotope spikes is required and potential isobaric interference effects from overlapping isotopes, metal oxides and other oxides formed in the plasma must be taken into account (McLauren et al., 1987). Whenever possible, the isotopes with least known isobaric interference are used. The mass bias effect must be monitored and corrected for, particularly for low mass isotopes.

3.1. Sources of error

The most significant errors of the measurements come not only from the random error of the ICP-MS magnified by the isotope-dilution calculation, but also from the variability of the mass bias effect and in some cases isobaric interference.

3.1.1. ID error propagation

Without a prior knowledge of the concentration, the spiked sample will have an isotope ratio that is different from the optimum ratio for isotope dilution determination (Webster, 1960). However, with the knowledge of concentration ranges expected in the sample, an estimate of the error magnification factor, M , can be made following the procedure described by Webster (1960). The random error on ratio measurement ($\sim 1\%$ for ICP-MS) is propagated to the error of the calculated concentration by factor M . For the samples analyzed so far, M rarely exceeds 2. Therefore, it is possible to achieve precision of 1–2% for samples analyzed within a single ICP-MS run.

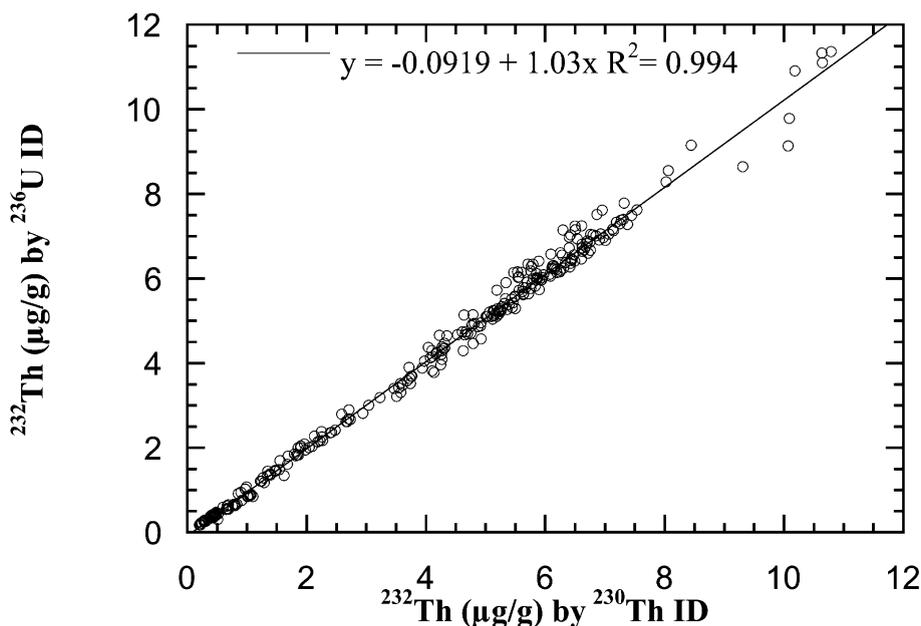


Fig. 1. Comparison of Th concentration results obtained by ^{230}Th ID and ^{236}U pseudo ID ICP-MS on sediment samples from several Southern Ocean cores and the Santa Barbara Basin. The agreement between the two methods is excellent. Two sigma errors of the measurements are about the size of the symbols.

3.1.2. Mass bias effect

It was observed that within a single ICP-MS run, the mass bias factors vary very little, again, making it possible to achieve a precision of 1–2%. However, there are substantial changes of 1–2% over a long period of time. The authors chose to monitor this effect by analyzing SPEX ICP-MS standards of Mo and Cd with natural abundance and the U-500 standard with a $^{235}\text{U}/^{238}\text{U}$ ratio of 0.9997. The mass bias is about 3% per amu for Mo, 2% per amu for Cd and 0.5% for U. The mass bias factors, defined as the true isotopic ratio divided by the measured background-corrected isotopic ratio, are 1.115 ± 0.026 ($n=25$) for $^{95}\text{Mo}/^{98}\text{Mo}$, 1.042 ± 0.012 for $^{111}\text{Cd}/^{113}\text{Cd}$ ($n=12$) and 1.016 ± 0.021 for $^{235}\text{U}/^{238}\text{U}$ ($n=20$) over 9 months. The mass bias factor interpolated for $^{236}\text{U}/^{238}\text{U}$ is 1.010 ± 0.014 . Over the 9 months period, the relative standard deviations (RSD) of mass bias factor are 2.3% for $^{95}\text{Mo}/^{98}\text{Mo}$, 1.1% for $^{111}\text{Cd}/^{113}\text{Cd}$ and 1.4% for $^{236}\text{U}/^{238}\text{U}$. Therefore, assessing the variability of the mass bias effect is important for long term reproducibility.

3.1.3. Isobaric interferences

The isobaric interferences for Mo isotopes were investigated. Three replicates of unspiked MC-E Pb6 yield a $^{95}\text{Mo}/^{98}\text{Mo}$ ratio of 0.623 ± 0.015 . The ratio becomes 0.673 after the mass bias factor of 1.08 is corrected for, which is slightly higher than the natural $^{95}\text{Mo}/^{98}\text{Mo}$ ratio of 0.6598. The excess count rate at mass 95 for 11 analyses of unspiked MC-E Pb6 has an average value of 800 ± 200 cps, when the contribution of Mo to the mass 95 count rate is estimated by the count rate obtained on mass 98 multiplied by the natural mass bias-corrected $^{95}\text{Mo}/^{98}\text{Mo}$ ratio. Given that the count rate on mass 95 in the sample spiked with ^{95}Mo is at 50,000 cps, the interference at mass 95, possibly due to BrO^+ or other unidentified polyatomic ion(s), is determined to be insignificant. Here, a correction of $\sim 1.6\%$ is ignored. Interference at mass 95 by BrO^+ should be reduced substantially by the digestion procedure, which oxidizes Br^- to volatile Br_2 . Isobaric interference from ^{98}Ru (abundance 1.9%) is insignificant because of the low abundance of Ru in marine sediments. For that same reason, $^{100}\text{Mo}/^{98}\text{Mo}$ ratios have been used as the spike/reference isotope pair for quantification of Mo in marine sediment reference materials, even though there is an isobaric interference from ^{100}Ru (McLauren et al., 1987). It was found that the contribution of ^{94}Zr to the total count rate on mass 94 exceeds 50% for a typical marine sediment sample (MC-E Pb6) spiked with ^{94}Mo , making ^{94}Mo an unsuitable isotope spike even though it was the spike of choice for seawater Mo ID ICP-MS analysis.

Isobaric interference from ^{113}In on ^{113}Cd is also insignificant and not corrected for. ^{113}In often contributes

only 35 cps to a typical total count rate in the range of 1000 to 3000 cps on mass 113 (Fig. 2). For about 75% of samples analyzed, this correction is less than 2%. The ^{113}In contribution is estimated from ^{115}Sn -corrected ^{115}In counts, where the ^{115}Sn count rate is estimated from the ^{120}Sn count rate assuming the natural $^{115}\text{Sn}/^{120}\text{Sn}$ ratio. The ICP-MS background on mass 113 varies from 20 to 30 cps. Any correction near the instrument background level is difficult and thus considered to be insignificant. However, monitoring ^{115}In and ^{120}Sn is highly recommended and a correction can be applied if the ^{113}In contribution to the 113 mass count rate exceeds 5%.

Polyatomic interferences on ^{111}Cd and ^{113}Cd are also insignificant and not corrected for. Metal oxide (^{95}MoO) and hydroxide ($^{94}\text{ZrOH}$ and $^{94}\text{MoOH}$) interference at m/z 111 is relatively minor (Cook et al. 1997), contributing to less than 0.5% of the count rate for the spiked sediment samples estimated by monitoring ^{90}Zr , ^{95}Mo and ^{98}Mo . Polyatomic interferences on ^{113}Cd are less than 1% of the count rate for the samples analyzed. In the present case, corrections of polyatomic interferences will lead to a lowering of calculated Cd concentration by at most 1.5%.

In other applications, ^{114}Cd is used for quantification due to its higher abundance (Lea and Martin, 1996). However, the authors found that the count rate on mass 114 has a significant and variable contribution from ^{114}Sn (monitored through ^{120}Sn), which varies from 3% to greater than 10% of the total count rate. Although ^{114}Cd can be used for calculating the Cd concentration after the Sn interference is corrected for, the precision is poorer.

No significant isobaric interferences for ^{236}U , ^{238}U and ^{232}Th , have been observed.

3.2. Accuracy and reproducibility

Analyses of the certified sediment/rock standard reference material (SRM) yielded results in excellent agreement with reported values for U, Th, Mo and Cd (Table 1). A quality control standard, MC-E Pb6, a sediment sample from Santa Barbara Basin, was used in assessing long-term precision. The U, Th, Mo and Cd concentrations are reproducible within 3–5% over 9 months of repeated analyses of MCE-PB6 (Table 1). Because the procedural blank proved to be generally higher than the ICP-MS background, the practical detection limit is defined here as being 3 times the RSD of the procedural blank over a 9-month period. These values upon calculation turn out to be 31 pg Mo/g, 39 pg Cd/g, 14 pg U/g and 32 pg Th/g, which equal 0.06 ppm Mo, 0.08 ppm Cd, 0.03 ppm U and 0.06 ppm Th, respectively, when the sediment sample size is 10 mg and the volume of 1% HNO_3 used to dissolve the digested sediment is 20 ml.

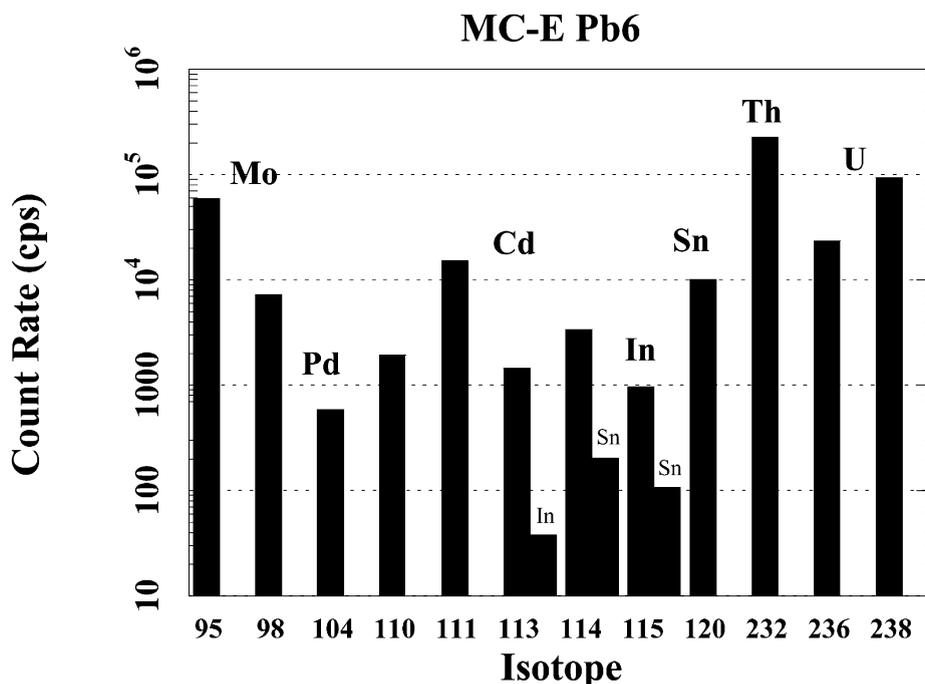


Fig. 2. ICP-MS results in total count rate for an analysis of 12.631 mg of acid digested marine sediment, MC-E-Pb6. The solid bar is the total count rate expressed as cps (counts per second) on each mass unit. ⁹⁵Mo, ¹¹¹Cd, and ²³⁶U are spike isotopes. The light shaded bars are the contribution of Sn on mass 114 and 115 based on count rate measured on ¹²⁰Sn and the contribution of In on mass 113 based on count rate measured on ¹¹⁵In corrected for ¹¹⁵Sn.

3.2.1. Comparison with ²³⁰Th ID ICP-MS analysis

Using ²³⁶U as a spike for ²³²Th measurement is justified by the excellent agreement obtained from many analyses of sediment samples from several Southern Ocean sediment cores and the Santa Barbara Basin by direct ²³⁰Th ID and pseudo ²³⁶U ID ICP-MS (Fig. 1). This agreement could be explained by a similarity in the first ionization energies of U (584 kJ/mol) and Th (587 kJ/mol). Several reasons made the authors prefer ²³⁶U over ²³⁰Th as a spike. The primary one being that ²³⁶U is more readily available and less radioactive than ²³⁰Th. In addition, a ²³⁰Th spike requires more frequent calibration due its strong affinity for sorption to surfaces. Eight analyses of a Southern Ocean sediment core sample V14-65 from 120 cm depth over 4 months gave Th concentrations of 3.72 ± 0.06 ppm and 3.58 ± 0.36 ppm, based on ²³⁰Th ID and ²³⁶U ID, respectively. Although the difference of Th concentration obtained by the two methods is within one sigma error, long term precision achieved by ²³⁰Th ID is better. Fifteen analyses of MC-E Pb6 over a 1-year period gave a Th concentration of 10.61 ± 0.46 ppm, calculated based on ²³⁶U ID. Three analyses of MC-E Pb6 gave a Th concentration of 9.83 ± 0.44 , calculated based on ²³⁰Th ID. It was concluded that ²³⁶U ID is only appropriate for applications when 5% precision on Th concentration is sufficient. For more precise work, ²³⁰Th ID is recommended.

The only considerable offset beyond the range of 5% precision is the Th concentration obtained on one SRM, AGV-1, which is about 10% too low compared to the reported value (Table 1).

3.2.2. Comparison between ID and standard addition for Mo

A standard addition test was performed on quality control sample MC-E Pb6. Variable amounts (0, 3.9, 17.8, 18.2 mg) of a dilution or a SPEX ICP-MS standard Mo solution, containing 1 µg Mo/g together with an internal In standard, were added to 4 aliquots of internal standard sediment MC-E Pb6. Due to the sample weight differences of MC-E Pb6 in this experiment, the ⁹⁸Mo count rate had to be normalized to sample weight after it was drift corrected via In normalization. The count rate on ⁹⁸Mo is proportional to the total amount of Mo in the sample, including both the sediment and the standard:

$$\text{Count rate} = \lambda \times (c_{\text{sed}} \times WT_{\text{sed}} + c_{\text{std}} \times WT_{\text{std}}) \quad (1)$$

where λ is the proportional factor, c is the concentration for Mo in µg/g and WT is the weight of sediment sample or standard in mg. Rearranging the above equation:

Table 1
Measured concentrations in standard reference materials

	ID ICP-MS ($\mu\text{g/g}$)	<i>n</i>	Reported value ($\mu\text{g/g}$)	Internal standardization ICP-MS ^a ($\mu\text{g/g}$)	<i>n</i>	ID ICP-MS Nameroff, 1996 ($\mu\text{g/g}$)
<i>Sample name</i>		<i>n</i>			<i>n</i>	
MESS-1	Mo 2.23±0.12	2				
	Cd 0.68±0.03	2	0.59±0.10	0.69±0.09	2	0.63±0.40
NBS	Mo 3.75±0.28	2				
SRM2704	Cd 3.34±0.12	2	3.45±0.22	3.30±0.09	4	
AGV-1	Mo 2.02±0.02	5		2.26±0.26	5	
	U 1.84±0.05	5	1.92	1.90	7	
	Th 5.92±0.06	5	6.5	6.33	7	
BCR-1	Mo 1.52±0.03	5	1.6	1.62	14	
	U 1.66±0.01	5	1.75	1.65	15	
	Th 5.86±0.06	5	5.98	5.97	15	
MC-E Pb6	Mo 2.57±0.11	15				
	Cd 1.12±0.05	7				
	U 4.64±0.05	15				
	Th 10.61±0.46	15				

^a Results of MESS-1 and NBS SRM2704 were reported by Chillrud (1996); results of AGV-1 and BCR-1 were measured by Dr. C. Langmuir's group at Lamont.

$$\frac{\text{Count rate}}{WT_{\text{sed}}} = \lambda \times c_{\text{sed}} + \lambda \times \frac{c_{\text{std}} \times WT_{\text{std}}}{WT_{\text{sed}}} \quad (2)$$

A regression performed on the sediment sample weight, normalized count rate, and normalized added Mo standard weight (Fig. 3) yields the slope and intercept which can be used to calculate the sediment Mo concentration:

$$c_{\text{sed}} = \frac{\text{intercept}}{\text{slope}} \times c_{\text{std}} \quad (3)$$

Based on the above standard addition calculation, the Mo concentration of MC-E Pb6 is 2.47 ppm, in good agreement with the long term running mean by Mo ID analyses of 2.57±0.11 ppm ($n=15$). This result suggests not only that the concentration of the ⁹⁵Mo enriched spike is well calibrated against the Mo standard solution, but that pertinent recoveries of the Mo standard added to the sediment samples are also achieved.

4. Application in marine geochemistry

The study site (Fig. 4) in Chesapeake Bay is located in a mesohaline region at the mouth of the Patuxent River, south of the sites where intensification of anoxia has been observed (Adelson et al., 2001; Officer et al., 1984; Tuttle et al., 1987; Zimmerman and Canuel, 2000). The bay's watershed, home to ~15×10⁶ people, accounts for more than half of the United States catch of blue crabs (Reshetiloff, 1995). Intensification of spring and summer anoxia within the past few decades may be responsible

for declining populations of benthic organisms and seagrasses, threatening the well-being of the entire ecological system (Reshetiloff, 1995). Although the intensification of seasonal anoxia in the bay is often attributed to eutrophication (Cooper and Brush, 1991; Cornwell et al., 1996), it is noteworthy that the worst anoxia observed in 1996 occurred when the bay was deluged with a record freshwater discharge (USGS, 1997). Therefore, it appears that the bay's oxygenation condition responds not only to nutrient forcing, but also to changes in freshwater runoff and stream discharges that affect surface water salinity as driven by climate variability (Cronin et al., 2000).

To resolve whether climate played a role in the recent intensification of seasonal O₂ depletion, the same shallow mesohaline bay sediments studied by Cronin et al. (2000) were used. The sediments were sectioned from cores PTXT2G4 and PTXT2P5, which were collected in 1996 aboard the R/V Discovery. PTXT2P5 (38°20.001'N, 76°18.580'W), was collected using a piston coring device at a water depth of 12 m, and core PTXT2G4 (38°19.588'N, 76°23.540'W), a gravity core, was collected from a water depth of 11.5 m. The average sedimentation rate based on ²¹⁰Pb is high, at 900 cm/ka, with the piston core PTXT2P5 containing sediments extending back to the 14th century, and the gravity core PTXT2G4 spanning ~80 a. Cronin et al. (2000) reconstructed bottom water salinity associated with wet/dry climate cycles from the abundance of the benthic foraminifera *Elphidium* based upon its bottom water tolerance to salinity.

Some of the same sediment intervals used in the bay's paleosalinity reconstruction were analyzed for Mo, Cd,

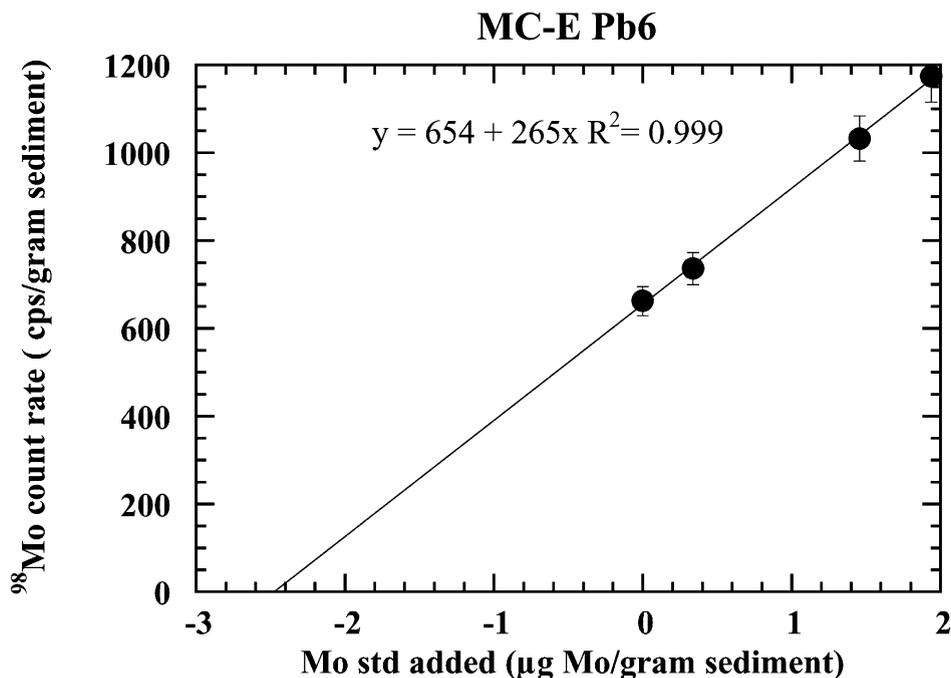


Fig. 3. Mo standard addition test on marine sediment sample, MC-E Pb6. Drift corrected count rate (cps) on ^{98}Mo normalized to per gram of sediment is plotted against the amount (μg) of Mo standard added normalized to per gram of sediment. Concentration of Mo obtained from standard addition is 2.47 ppm by extrapolated to zero intercept. Fifteen analyses of MC-E Pb6 by ^{95}Mo ID give Mo concentration of $2.57 \pm 0.11 \mu\text{g/g}$.

U, and Th. Excess metals were calculated assuming that crustal background is represented by average shale metal to thorium ratios (Taylor and McLennan, 1985) and then computed as follows:

$$\text{Metal}_{\text{excess}} = [\text{Metal}_{\text{sample}}] - [(\text{MetalTh})_{\text{crustal}} \times Th_{\text{sample}}] \quad (4)$$

Concentrations of excess Mo and Cd show repeated oscillations that are inversely correlated with paleosalinity variation in the 20th century deposition for the mesohaline section of the bay (Fig. 5, PTXT2G4). For two wet-periods dated to the early 1600s and early 20th century (Fig. 5, PTXT2P5), Mo and Cd displayed distinct peaks with similar amplitudes of enrichment as those found in the 20th century fluctuations. On the other hand, excess U showed little fluctuation over time for both pre- and post-industrial records.

The same magnitude of excess Mo and Cd enrichment corresponding to each wet period in pre- and post-industrial records (Fig. 5) suggests that the mesohaline region of the bay has anoxic conditions that fluctuate naturally with climate and freshwater influx over time. The linkage between the central bay's bottom water redox state and climate lies in how the bottom water is ventilated: less freshwater discharge sets forth a low

halocline density gradient enhancing ventilation (Reimers et al., 1990; Taft et al., 1980), while periods of increased discharge magnify the gradient and inhibit ventilation within the bay (Cronin et al., 1999). Anoxia following an extreme discharge in 1984 caused detectable levels of dissolved sulfide in the bay's bottom water (Seliger et al., 1985). The source of the sulfide is from high concentrations of sulfide (up to $600 \mu\text{M}$) diffusing within sediment pore water during the late summer (Roden and Tuttle, 1992). High levels of sulfide in sediment pore water undoubtedly promote authigenic Mo (Adelson et al., 2001; Colodner, 1991; Zheng et al., 2000) and Cd precipitation (van Geen et al., 1995). Hence, more authigenic Mo and Cd will be precipitated during events of intensified anoxia.

It also appears that at these particular sites cultural eutrophication has not been a major factor in contributing to the variation of anoxia as recorded by Mo and Cd with time. A large fraction of excess U in Chesapeake Bay sediment is of surface water particulate origin (Shaw et al., 1994). Preservation of particulate non-lithogenic U in marine sediments is enhanced when bottom water O_2 concentrations are low (Zheng et al., 2002). Therefore, relatively constant excess U concentrations (Fig. 5) indicate that the surface water derived U, or biological productivity, has not changed significantly over time at these depths within the mid-region portion

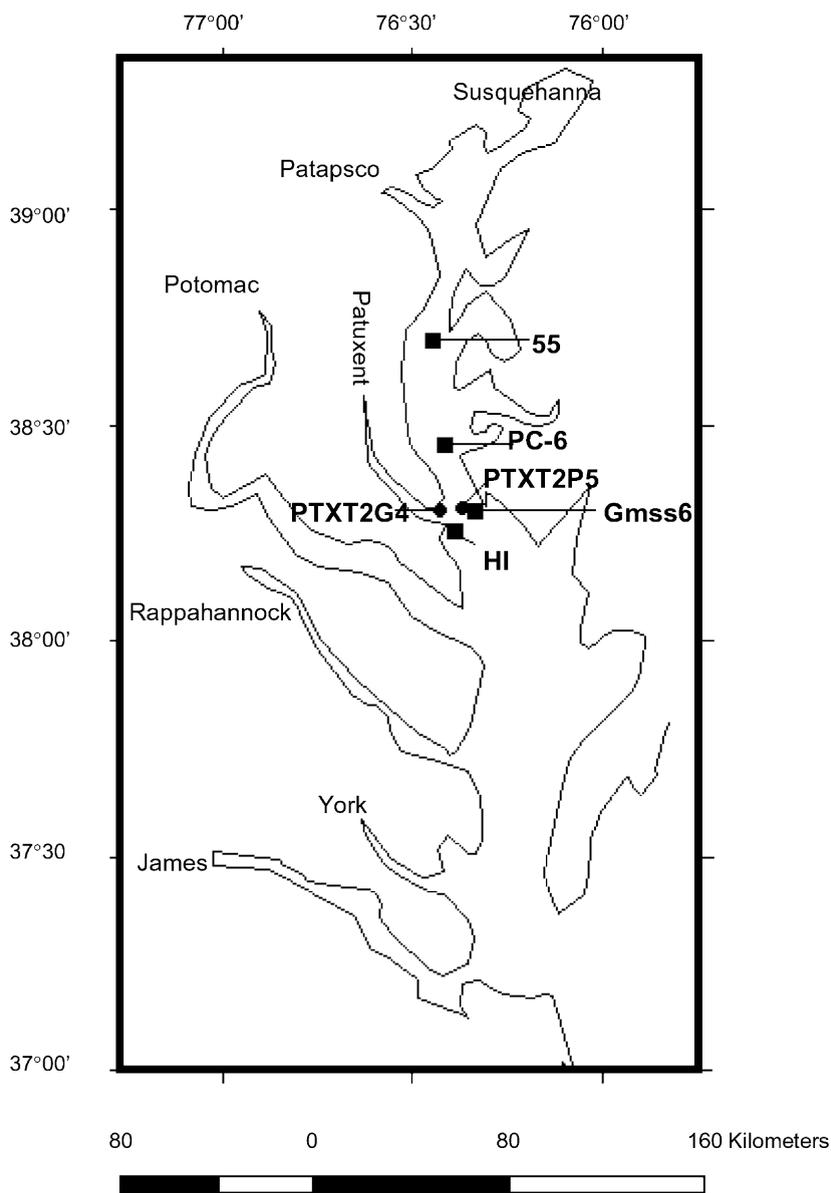


Fig. 4. Locations of cores PTXT2G4 and PTXT2P5 from Chesapeake Bay used in this study, along with locations of cores PC-6, 55, Gmss6, (Adelson et al., 2001), and HI, (Cornwell, et al. 1996), used in previous investigations of anoxia within Chesapeake Bay.

of the bay, although the deeper channels of the bay still merit additional study.

In addition, it is interesting to note that in the same core, PTXT2G4, Cd enrichment observed to occur around year 1940 is not coupled with an increase in authigenic Mo (Fig. 5). This Cd intensification coincides with a peak in organic C:N ratio as recorded in core HI (Fig. 4) from the midbay for the 1940s (Cornwell et al., 1996). In addition, the 1940s coincides with a wave of farm abandonment (Zimmerman and Canuel, 2000) and urbanization that took place within the area (Brush, 1984). This suggests that the enrichment of Cd for this

time may be allochthonous accumulations of a refractory fraction of biogenic Cd in the sediments even though the bottom waters were oxic at the time. Alternatively, the low C:N ratio observed by Cornwell et al. (1996), and the low $^{187}\text{Os}/^{188}\text{Os}$ ratios found within the center of the bay corresponding to the 1940s (Helz et al., 2000) indicate that the anomalous Cd peak may have been instigated anthropogenically.

When placed in context with earlier studies, the results also elucidate some of the questions regarding periods of anoxia within the bay. Previous studies concerning anoxia within the bay by Officer et al. (1984)

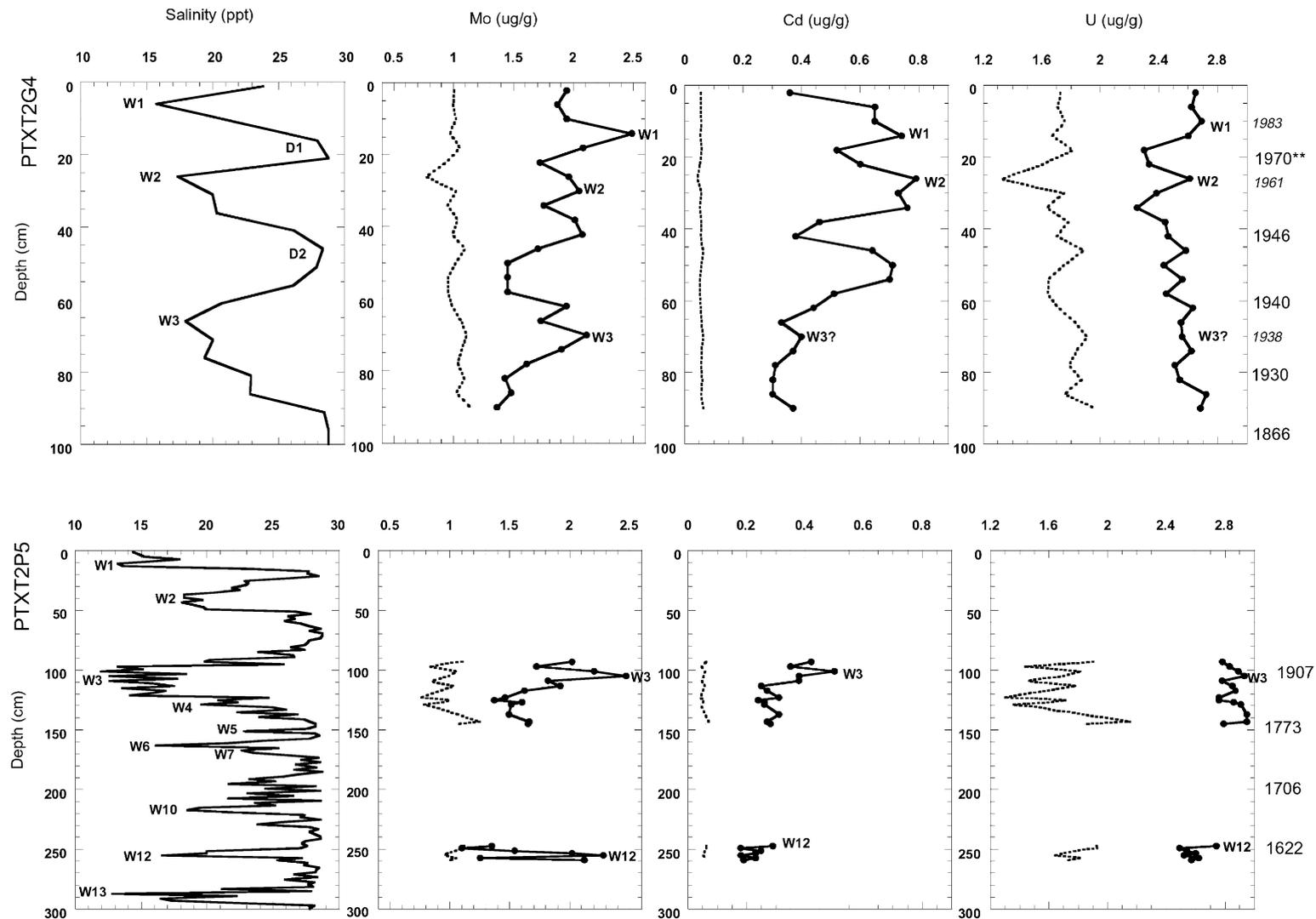


Fig. 5. Depth profiles of paleosalinity, Mo, Cd, and U for two cores, gravity core PTXT2G4 (11.5 m) and piston core PTXT2P5 (12 m), near the mouth of the Patuxent River in the mid region of Chesapeake Bay. Concentrations are also plotted vs. time and show the paleoanoxia reconstruction of the midbay area. The thin dotted lines indicate the detrital background levels of Mo, Cd, and U estimated using average shale metal to Th ratios (Taylor and McLennan, 1985). Italicized years show the relationship between wet periods and enhanced enrichments of excess Mo, Cd, and U in core PTXT2G4.

and Seliger and Boggs (1988) show conflicting trends in post-industrial deoxygenation patterns (Adelson et al., 2001). In investigating this discrepancy, Adelson et al. (2001) found increasing authigenic Mo enrichments in the northern section of the bay (north of PC6 at $\sim 38.5^\circ\text{N}$, Fig. 4) concentrated within sediments from the latter half of the 20th century. The present results at a location about 25 km south of PC6, however, did not show any increase in peak authigenic Mo concentrations for the same period of time. A small secular trend of increasing low level Mo values post-1940s (Fig. 5) is observed, although more analyses on different cores from the same region are needed to confirm this trend.

How do we reconcile the oxygenation history reconstructed for the bay based on authigenic Mo at various locations in the bay? One explanation is that anoxia intensity varies spatially with cultural eutrophication intensifying seasonal deoxygenation northward towards the head of the bay north of PC6 (Adelson et al., 2001). On the other hand, the anoxia intensity in the midbay (PTXT2G4 and PTXT2P5) is driven mostly by the freshwater discharge received in the area. The lack of an increase in U enrichment for the late 20th century in PTXT2G4 and PTXT2P5 (Fig. 5) is consistent with the notion that the mid-bay region has not experienced much influence of cultural eutrophication. The northern bay, including the Rhode River area north of cores 55 and PC6 near Parker Creek (Adelson et al., 2001), is the region of the bay most sensitive to deoxygenation. It is the first part of the bay to show O_2 depletion in the spring and the last to return to its initial oxygenated condition in the fall (USGS, 2000). Regions further down the bay closer to the Patuxent and Potomac Rivers are subjected to shorter durations or less extreme instances of anoxia as recorded in midbay cores Gmss6 (Adelson et al., 2001) and PTXT2. Therefore, the sediment authigenic Mo profiles found longitudinally traversing the bottom of the bay reflect the spatial extent of cultural eutrophication in recent decades.

5. Conclusions

A rapid method for simultaneous analysis of Mo, Cd, U and Th in marine sediment samples as small as 10 mg yields highly precise and accurate results. Because of the simultaneous measurements of all 4 elements of geochemical interest and the overall small sample size requirement, the analysis time is reduced by more than a factor of 30 compared to previous methods. The ID ICP-MS also offers a large dynamic range; therefore, it is particularly suitable when the expected range of sample concentration is large. This method also offers the flexibility of adding other elements of geochemical interest in the future.

When applied to Chesapeake Bay, the authigenic Cd and Mo correlated to microfaunal proxies and indicated that bottom waters in the mesohaline section of the bay are less oxygenated when surface water salinity is lower. In addition, authigenic U levels remained almost constant through the same time periods, suggesting that particulate fluxes or biological productivity did not vary significantly. This implies that climate driven changes in discharge play a major role in determining the O_2 level in the bottom waters of the bay's mid region. In addition, the magnitude of paleo-oxygenation of the bay as recorded by Mo and Cd is similar for both pre-industrial and industrial periods of time. This suggests that other factors, such as inputs of N and P, play a secondary role in determining the O_2 level of the mesohaline section of the bay. The results, in conjunction with oxygenation reconstruction based on authigenic Mo at the northern section of the bay, suggest that the worsening of anoxia, possibly due to cultural eutrophication in recent decades, is restricted north of $\sim 38.5^\circ\text{N}$.

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